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Ultraviolet Absorption Coefficients of CO_2, CO, O_2, H_2O, N_2O, NH_3, NO, SO_2, and CH_4 Between 1850 and 4000 A

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Abstract

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The ultraviolet absorption coefficients have been determined for CO_2, CO, O_2, H_2O, N_2O, NH_3, NO, SO_2 and CH_4 in the wavelength region between 1850 and 4000 A. By using a double beam instrument and a 10 cm path length, sensitivities of 10^{-4} cm^{-1} were achievable in most cases, permitting a considerable extension of the literature data. AUTHOR

Introduction

Ultraviolet absorption coefficients reported in the literature fall, in general, into two categories: those determined at wavelengths below 1850 A and those determined at wavelengths above 2500 A. The intermediate region, between 1850 and 2500 A is of great interest in connection with photochemical studies of planetary atmospheres since the high intensities of the solar radiation and the long path lengths through the atmospheres may result in significant amounts of photochemical reactions even where the absorption coefficient is very small. The excellent work of Watanabe, Zelikoff, and Inn (1953) covers this wavelength range for many gases, but, in general, does not give values below 0.1 cm^{-1}. For these reasons the absorption coefficients of a number of gases which are known to be either major or minor constituents of various planetary atmospheres were determined.

Experimental

<u>Description of Apparatus:</u> Absorption experiments were carried out using a Perkin-Elmer Model 350 absorption spectrophotometer. This is a double beam instrument covering the spectral region from about 1850 A to 2.7 μ. For these studies measurements were made between 1850 and 4000 A. Using a 10 cm path length and a scale expansion of 50 it was possible to measure absorption coefficients as low as 10^{-4} cm^{-1}.

<u>Purification of Gases:</u> The gases studied were CO_2, CO, O_2, H_2O, NH_3, NO, N_2O, SO_2 and CH_4. Research grade CO_2 was purified from traces of air and water by fractional distillation. The research grade CO (assayed reagent) obtained from Air Reduction Co. was found to contain several hundred parts per million of iron carbonyl even though supplied in a glass flask. This was removed by successive frational distillations. Research grade NH_3 and SO_2 were used directly from cylinders or lecture bottles and the oxides of nitrogen were purified from any NO_2 contamination by fractional distillation. Distilled water was used for the H_2O measurements. Research grade CH_4 was purified from large amounts of CO_2 by fractional distillation.

Results

The results obtained for all gases except CH_4 are shown in Figures 1 through 8 which show the absorption coefficients as a function of wavelength. In each case the path length was 10 cm and the reference cell was filled with either N_2 or Ar. CO_2, CO, CH_4, and O_2 were measured at near atmospheric pressure. The H_2O pressure was 20 mm and the strongly absorbing gases NO, N_2O, NH_3, and SO_2 were measured at lower pressures. The pressures employed in each case are listed in Table I. For CH_4 no absorption could be detected, showing that the absorption coefficient is less than 10^{-4} cm^{-1} throughout the entire range investigated.

Discussion

The results for CO_2, CO, and O_2 (see Figures 1, 2, and 3) are discussed in detail elsewhere (Harteck, Reeves, and Thompson, 1963). For CO_2 it is found that absorption does occur in the wavelength region above 1750 corresponding to the spin-forbidden dissociation into ground-state products. CO exhibits absorption in this region only weakly in the narrow Cameron bands corresponding to the excitation to the $a^3\Pi$ level. The absorption coefficient of O_2 in the wavelength region between 2050 and 4000 A must be less than 10^{-4} cm^{-1} since no absorption was observed in this region.

H_2O shows continuously decreasing absorption for wavelengths longer than 1850 A. The present results complement those of Watanabe et al. (1953) and extend them by over two orders of magnitude as shown in Figure 4. Similar remarks apply to the continuous absorption by N_2O (Figure 5).

For NH_3, NO, and SO_2 (Figures 6, 7, and 8) which show band structure rather than continuous absorption, the values obtained for the absorption coefficients will vary with the instrumental resolution employed. Nevertheless reasonable agreement was found with the results of Watanabe et al. (1953) for NH_3 and NO and with those of Golomb, Watanabe, and Marmo (1962) for SO_2. The lack of absorption observed for CH_4 is in agreement with the results of Watanabe et al. (1953) since extrapolation of their data indicates that the absorption coefficient should be below 10^{-4} cm^{-1} at these wavelengths.

References

Golomb, D., K. Watanabe, and F. F. Marmo, Absorption Coefficients of Sulfur Dioxide in the Vacuum Ultraviolet, J. Chem. Phys. 36, 958, 1962.

Harteck, P., R. R. Reeves, Jr., and B. A. Thompsom,Photochemical Problems of the Venus Atmosphere, NASA TN D-1984, 1963.

Watanabe, K., M. Zelikoff, and E. C. Y. Inn, Absorption Coefficients of Several Atmospheric Gases, AFCRC Tech. Rpt. 53-23, 1953.

Table I

Gas Pressures Employed for Absorption Measurements

Gas	Pressure, mm.
CO_2	700
CO	660
O_2	720
H_2O	20
N_2O	326, 2050 - 4000 A 6, 1850 - 2050 A
NH_3	760, 2250 - 4000 A 100, 2250 - 4000 A 5, 1850 - 2150 A 0.1, 1850 - 2150 A
NO	6*
SO_2	5, 2000 - 4000 A 0.259; 1850 - 2200 A
CH_4	750

*NO was measured at low pressures to avoid interferences from dimerization.

List of Figures

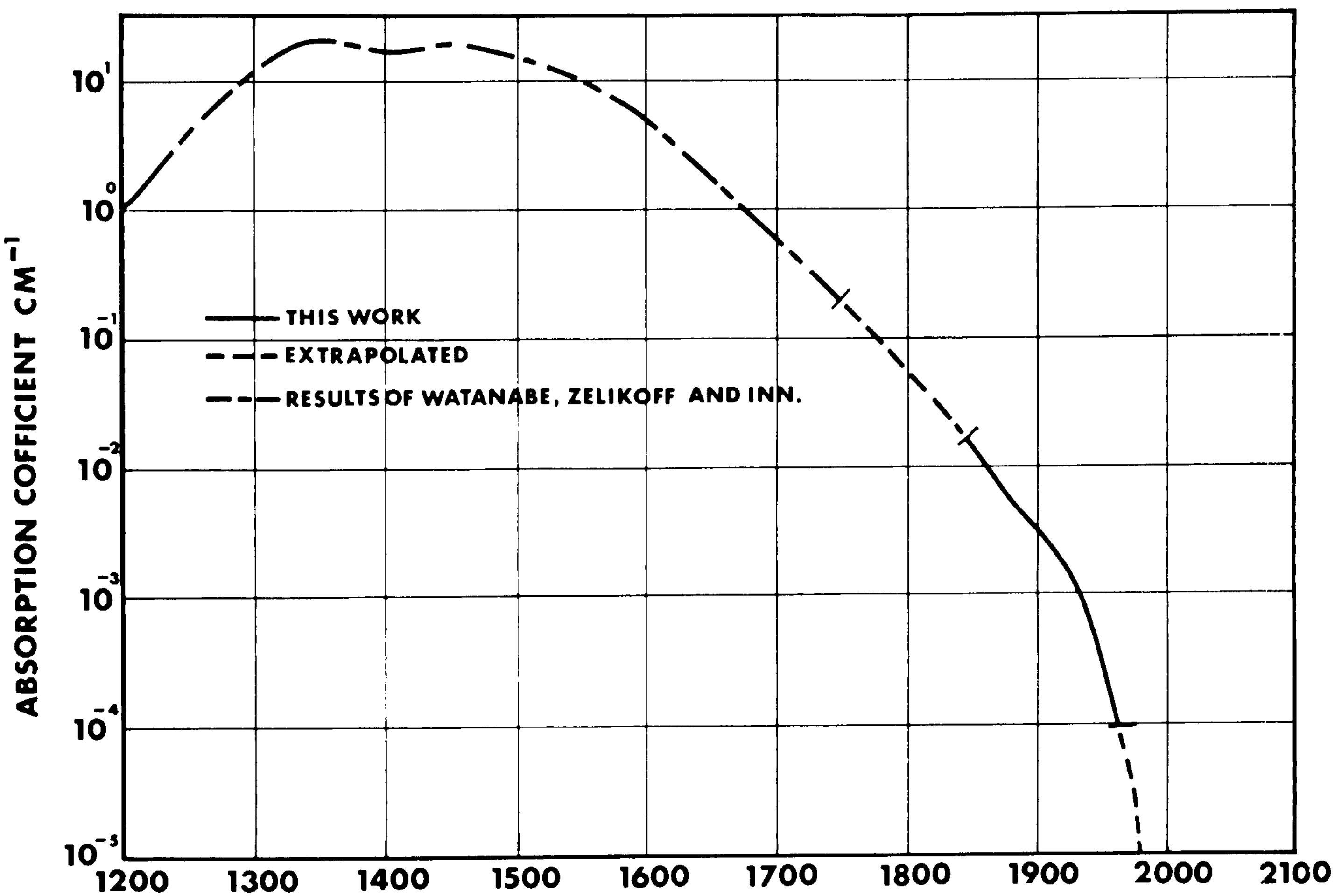

FIGURE 1
ABSORPTION COEFFICIENT OF
CO_2 AS A FUNCTION OF WAVELENGTH

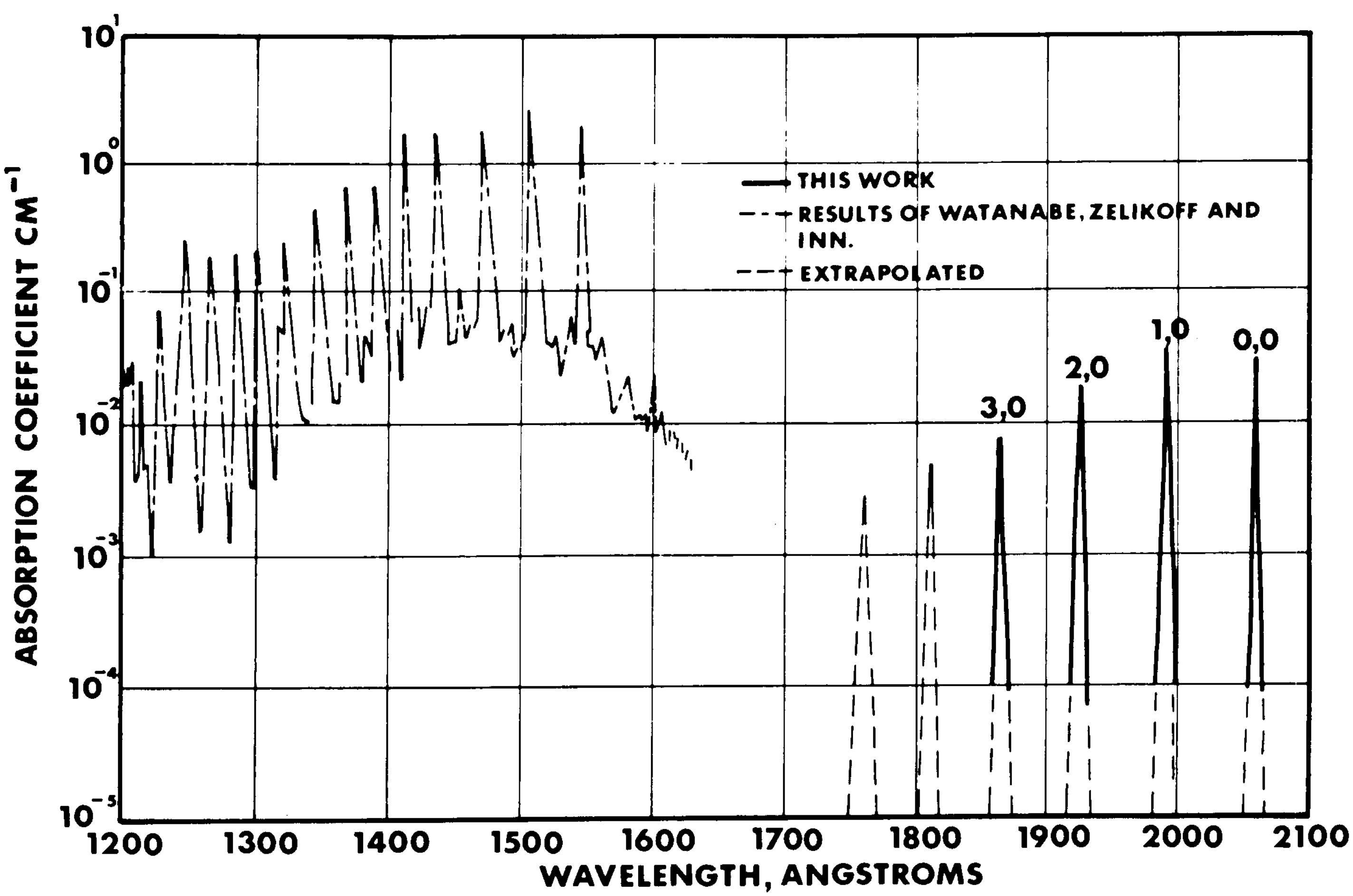

FIGURE 2
ABSORPTION COEFFICIENT OF
CO AS A FUNCTION OF WAVELENGTH

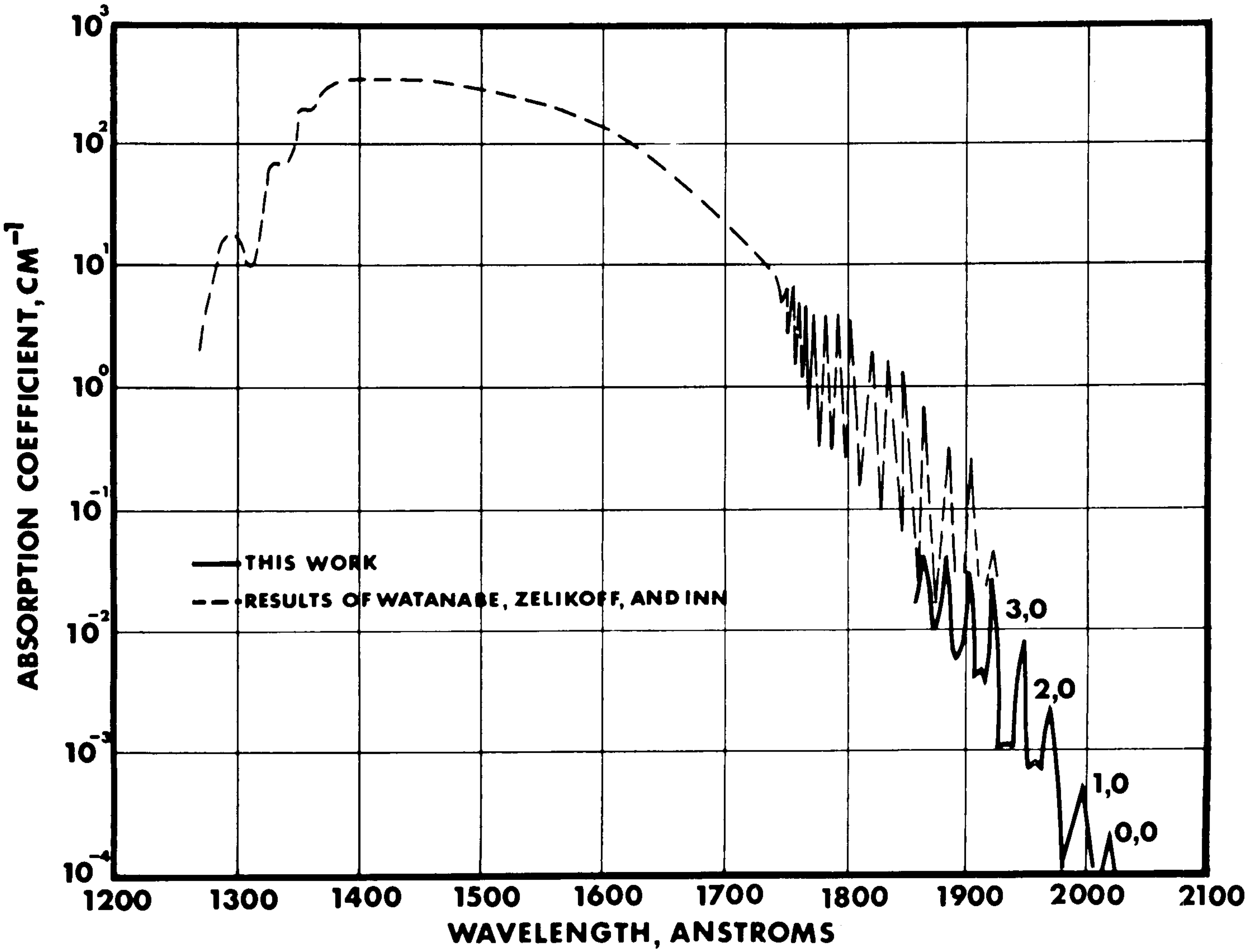

FIGURE 3
ABSORPTION COEFFICIENT OF
O_2 AS A FUNCTION OF WAVELENGTH

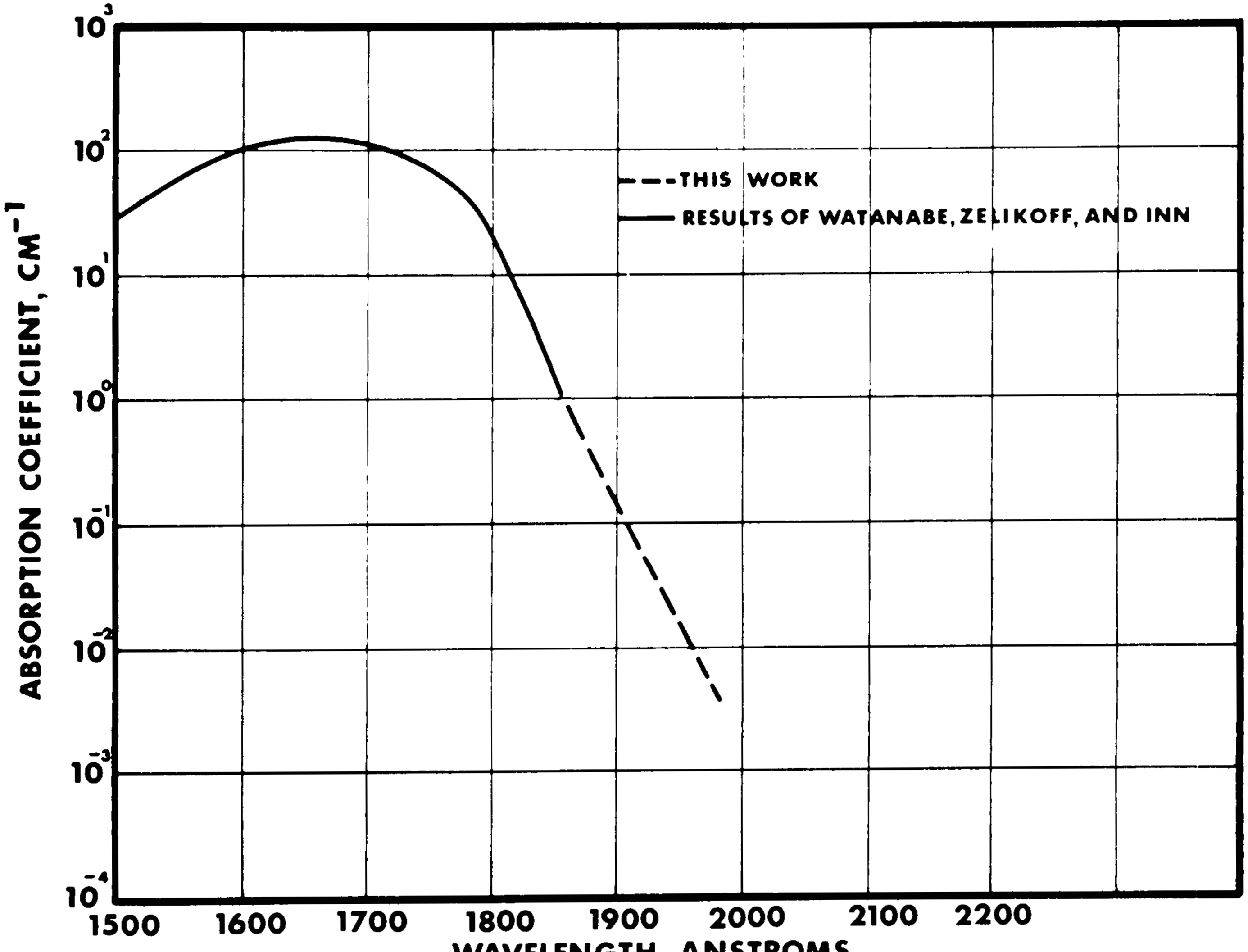

FIGURE 4
ABSORPTION COEFFICIENT OF
H_2O AS A FUNCTION OF WAVELENGTH

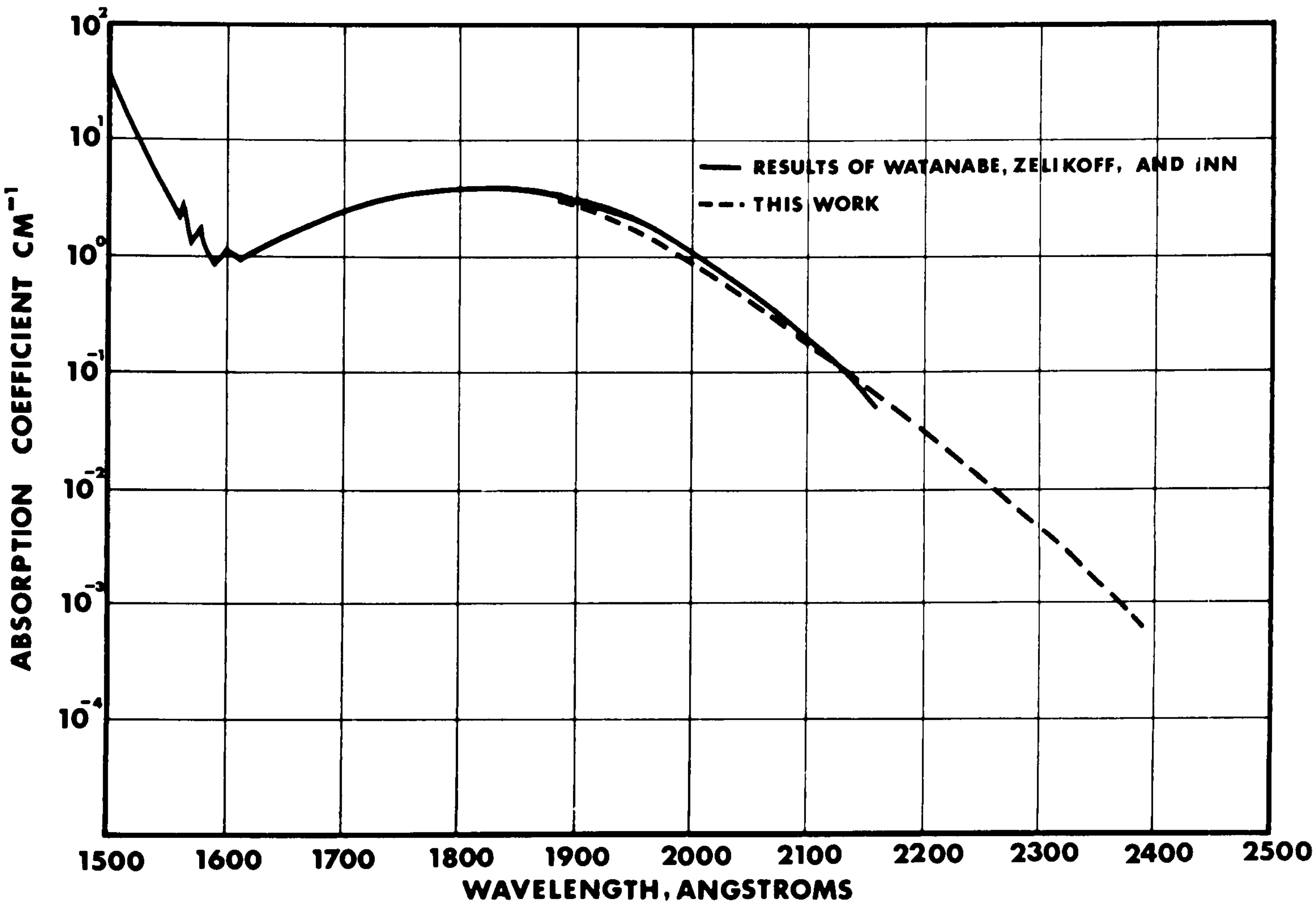

FIGURE 5
ABSORPTION COEFFICIENT OF N_2O AS A FUNCTION OF WAVELENGTH

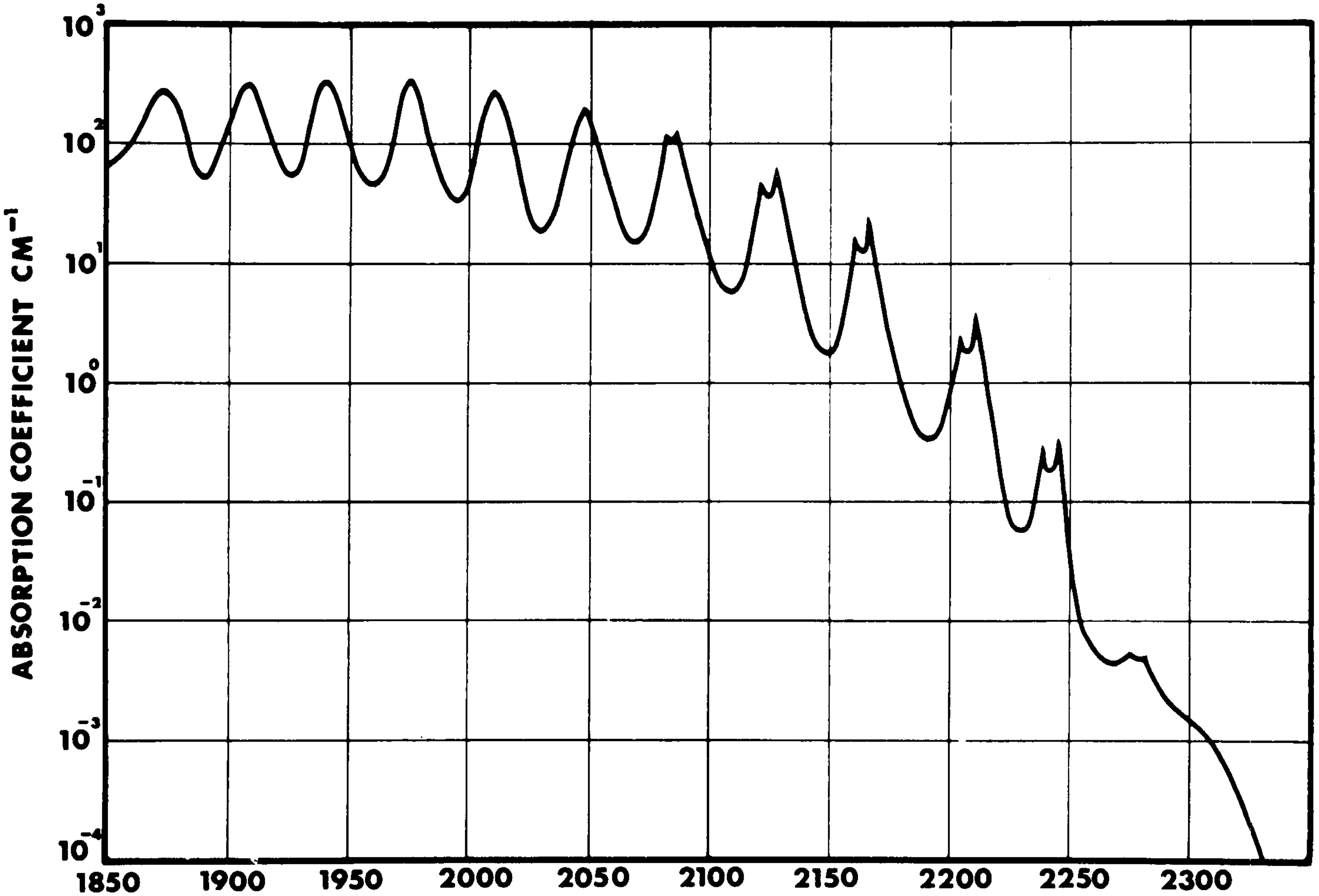

FIGURE 6
ABSORPTION COEFFICIENT OF
NH_3 AS A FUNCTION OF WAVELENGTH

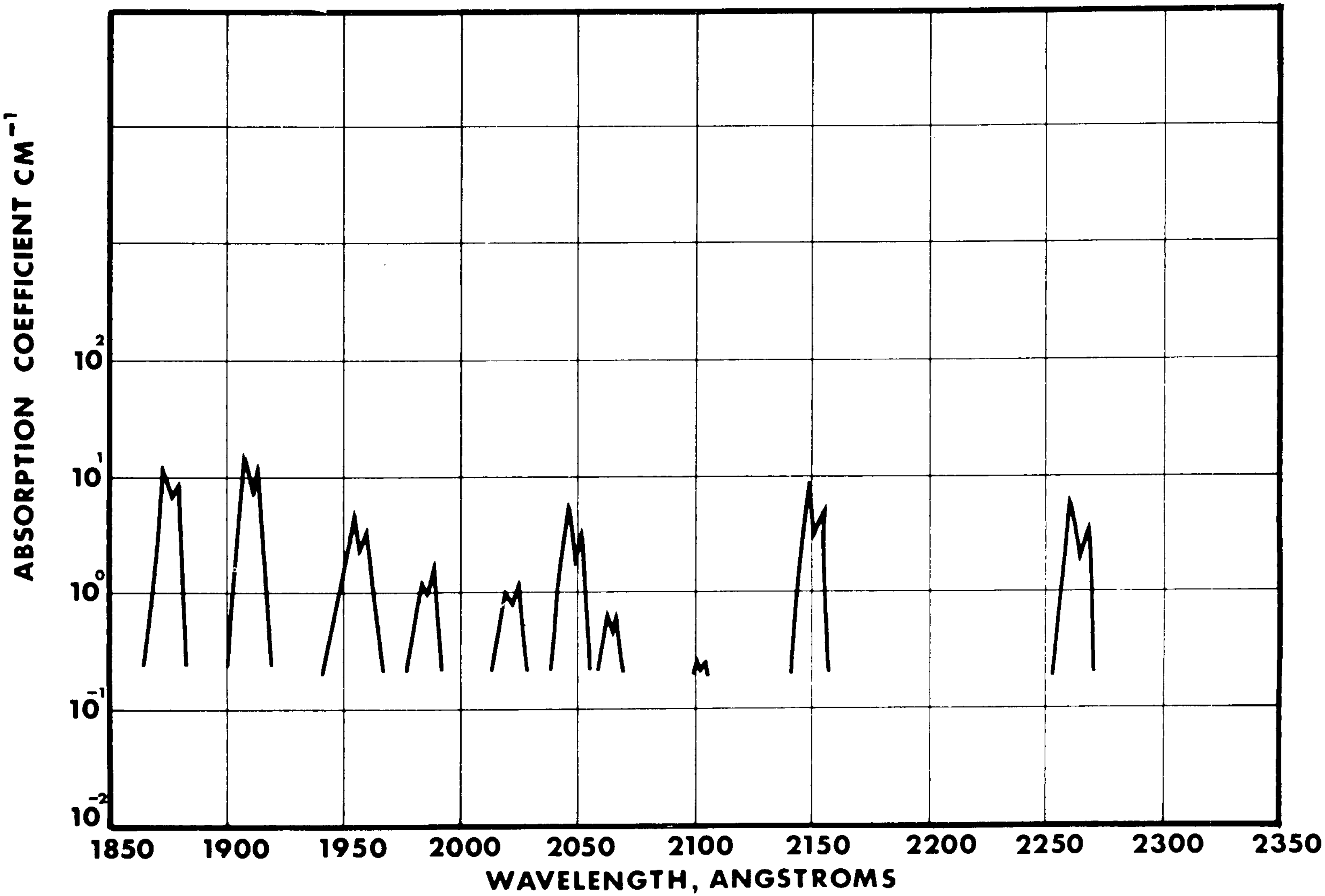

FIGURE 7
ABSORPTION COEFFICIENT OF NO
AS A FUNCTION OF WAVELENGTH

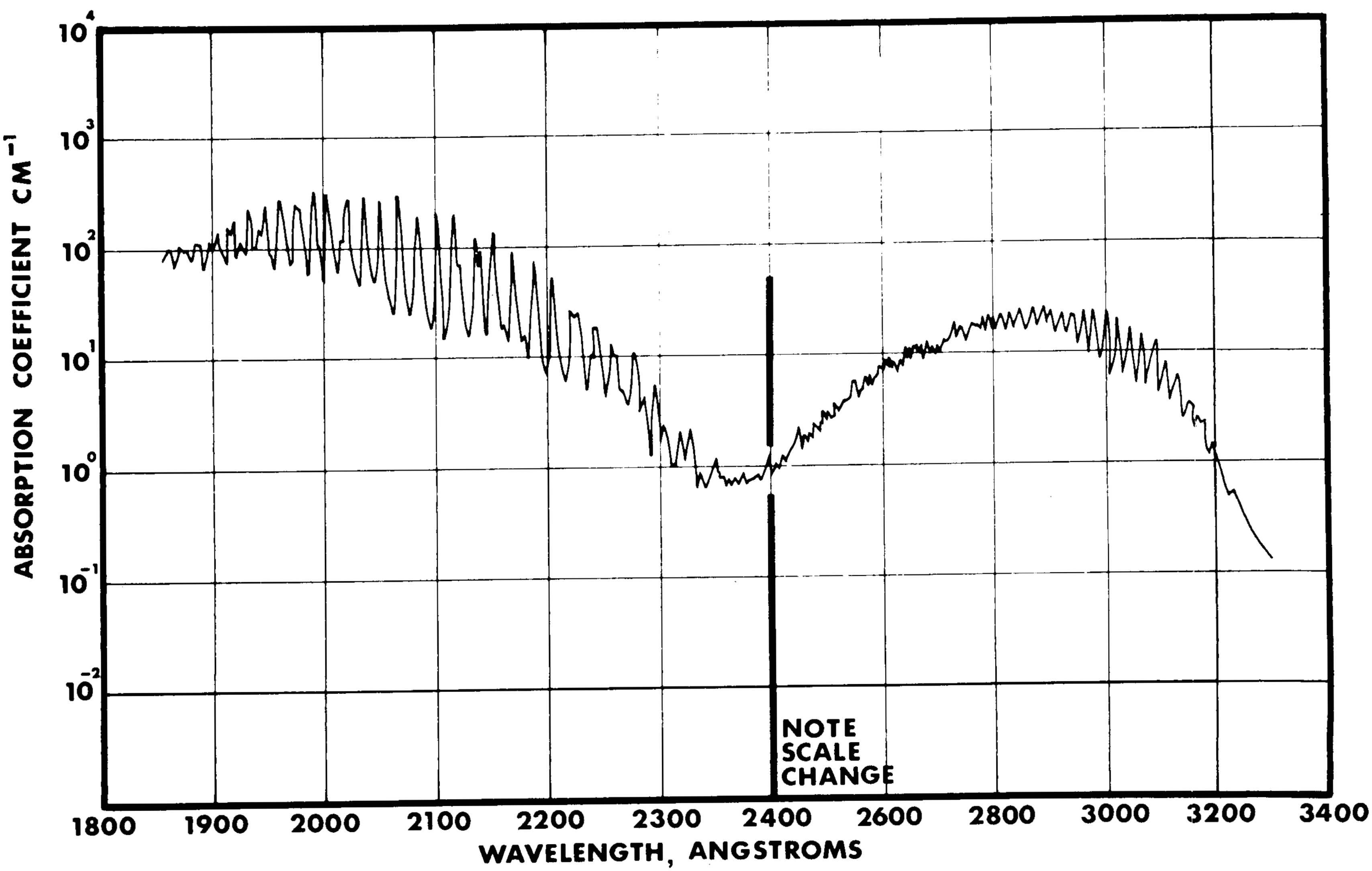

FIGURE 8
ABSORPTION COEFFICIENT OF
SO_2 AS A FUNCTION OF WAVELENGTH